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(54) Title: COMPOSITION

(57) Abstract: The present invention relates to a method of preparing a composition comprising mixing a silica sol having an S-value from about 5 to about 50 % and a mineral acid. The invention also relates to a composition obtainable by the method and a composition comprising a network of silica particles and mineral acid, wherein the silica particles have a particle size of from about 2 to about 7 nm. The invention also relates to the use of the composition as a gelled electrolyte.



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Composition

The present invention relates to a composition suitable for use as battery electrolyte, pickling gel, or binder of waste material, and a method of providing the composition.

5

Background of the invention

It is known in the art to provide battery electrolytes by mixing a gelling agent with sulphuric acid. The electrolyte is in the form of a thixotropic gel which as essential constituents includes sulphuric acid and a gel-forming agent which may be e.g. a silica sol as proposed in US 5,663,321. This type of gelled electrolyte involves several advantages over non-gelled liquid electrolytes such as the possibility of independent positioning while being substantially free of leaking and maintenance. However, the electrolyte disclosed in US 5,663,321 lacks sufficient gel strength and the time of gelling is often too long.

15 The present invention intends to provide a gelled composition which solves the above problems in batteries, and which also may be used for other applications.

The invention

The present invention relates to a method of preparing a composition comprising
20 mixing a silica sol having an S-value from about 5 to about 50 % and a mineral acid.

It has been found that the composition of this invention when applied as a gelled electrolyte in e.g. lead-acid batteries results in longer service life, shorter gelling time, and improved gel strength. When the silica sol and mineral acid have been mixed, gelling will take place. This is due to the fact that the colloidal silica particles present in the silica sol
25 will form siloxane bridges between each other in the presence of the mineral acid which leads to aggregation and gelling thereof.

According to a preferred embodiment, the silica sol has an S-value from about 8 to about 47, preferably from about 10 to about 45, even more preferably from about 15 to about 45, even more preferably from about 25 to about 43, and most preferably from
30 about 30 to about 40 %.

It has been found that an S-value within these ranges can optimise the mentioned advantages. The S-value characterises the extent of aggregation of colloidal silica particles, i.e. the degree of aggregate or microgel formation. The S-value has been measured and calculated according to the formulas given in "Degree of hydration of
35 particles of colloidal silica in aqueous solution", J. Phys. Chem. 60(1956), 955-957 by Iler, R.K. & Dalton, R.L.

The S-value depends on the silica content, the viscosity, and the density of the colloidal silica particles. The S-value represents the amount of SiO₂ in percent by weight present in the dispersed phase of the silica sol. The S-value can be controlled during the production process as further described in e.g. US 5368833.

5 The silica sol preferably has a silica content from about 5 to about 60, more preferably from about 7 to about 45, and most preferably from about 10 to about 30 wt%. The silica sol comprises silica particles which suitably have a specific surface area from about 400 to about 1200, preferably from about 500 to about 1000, and most preferably from about 600 to about 900 m²/g. The silica particles suitably have a particle size of from
10 about 2.5 to about 7, preferably from about 3 to about 6, and most preferably from about 4 to about 5 nm. Suitably, the silica sol and the mineral acid are mixed in a weight ratio of silica to mineral acid (counted as diluted mineral acid) from about 1:100 to about 25:100, preferably from about 2:100 to about 11:100, more preferably from about 2.5:100 to about 8:100, and most preferably from about 3:100 to about 6:100. The components are
15 preferably homogenously mixed to uniformly distribute the silica particles of the silica sol in the electrolyte.

Silica sols comprise colloidal silica particles which may be derived from e.g. precipitated silica, micro silica (silica fume), pyrogenic silica (fumed silica) or silica gels with sufficient purity, and mixtures thereof.

20 Colloidal silica particles and silica sols according to the invention may depending on the application of the composition be modified and can contain other elements such as amines, aluminium and/or boron, which can be present in the particles and/or the continuous phase. Boron-modified silica sols are described in e.g. US 2,630,410. The aluminium modified silica particles suitably have an Al₂O₃ content of from about 0.05 to
25 about 3, preferably from about 0.1 to about 2 wt%. The procedure of preparing an aluminium modified silica sol is further described in e.g. "The Chemistry of Silica", by Iler, K. Ralph, pages 407-409, John Wiley & Sons (1979) and in US 5 368 833.

The colloidal silica particles preferably have a narrow particle size distribution, i.e. a low relative standard deviation of the particle size. The relative standard deviation of
30 the particle size distribution is the ratio of the standard deviation of the particle size distribution to the mean particle size by numbers. The relative standard deviation of the particle size distribution preferably is lower than about 60 % by numbers, more preferably lower than about 30 % by numbers, and most preferably lower than about 15 % by numbers.

35 The colloidal silica particles are suitably dispersed in an aqueous solvent, suitably in the presence of stabilising cations, preferably K⁺, Na⁺, Li⁺ for battery electrolyte applications, but for other applications also e.g. NH₃, organic cations, primary, secondary,

tertiary, and quaternary amines, or mixtures thereof so as to form an aqueous silica sol. However, also dispersions comprising organic solvents e.g. lower alcohols, acetone or mixtures thereof may be used for applications other than battery electrolytes, suitably in an amount of from about 1 to about 20, preferably from about 1 to about 10, and most preferably from about 1 to about 5 volume percent of the total solvent volume. However, aqueous silica sols without any further solvents are preferably used. The pH of the silica sol suitably is from about 1 to about 13, preferably from about 6 to about 12, and most preferably from about 7.5 to about 11. However, for aluminium-modified silica sols, the pH suitably is from about 1 to about 12, preferably from about 3.5 to about 11. Preferably, the silica sol has an iron content lower than about 100 ppm by weight since iron may cause discharge of batteries in which the composition of this invention may be used and can shorten battery life times. More preferably, the iron content is lower than about 50, and most preferably lower than about 30 ppm by weight. Preferably, the content of chloride in the silica sol is lower than about 50, more preferably lower than about 30, and most preferably lower than about 10 ppm by weight. The low chloride content is essential in the formed composition (in battery applications) since grid corrosion, i.e. corrosion of the lead grid in the battery then can be reduced. Other impurities present in the composition that can be detrimental and their acceptable levels should not exceed prescribed limits.

Preferably, the mineral acid, which serves as electrolyte, is hydrochloric acid, nitric acid, phosphoric acid, sulphuric acid, and mixtures thereof, most preferably sulphuric acid, particularly for any battery application. The concentration of the mineral acid, especially sulphuric acid, suitably is from about 5 to about 99, preferably from about 20 to about 80, and most preferably from about 30 to about 60 wt%. A too low concentration will result in a bad electrolyte (with low conductivity) and long gel time. Suitably, the pH of the mineral acid is from about -2 to about 2, preferably from about -1.5 to about 1, more preferably from about -1 to about 0.5, and most preferably from about -0.5 to about 0. A suitable concentration of the mineral acid can be achieved by diluting a concentrated mineral acid with water. Suitably, sulphuric acid (as used mineral acid) has a density from about 1.04 to about 1.8, preferably from about 1.15 to about 1.75, more preferably from about 1.2 to about 1.5, and most preferably from about 1.3 to about 1.4 kg/dm³.

Preferably, the mixing of silica sol and mineral acid is performed at a temperature from about 0 to about 95, preferably from about 5 to about 50, and most preferably from about 10 °C to about 35 °C. Dilution of sulphuric acid and other mineral acids often leads to an increase in temperature due to the exothermic reaction taking place. Therefore, the diluted acid used preferably is precooled to a temperature below room-temperature. The mixing time of silica sol and mineral acid suitably is from about

100 milliseconds to about 30 minutes, preferably from about 100 milliseconds to about 10 minutes, and most preferably from about 100 milliseconds to about 1 minute. The silica sol and the mineral acid preferably are mixed in an in-line mixer, e.g. a static mixer, just before filling it into a battery cell or other use. A too long mixing time is detrimental to the gel strength while a too short mixing time may lead to insufficient mixing.

Further components which may be added to form the composition of the present invention include orthophosphoric acid, suitably to a concentration of from about 1.5 to about 5% by weight with respect to the total weight of the forming composition (gel) in order to increase the conductivity as well as the cycle and discharge resistance of a battery.

Sodium sulphate may also be added in an amount of from about 1 to about 25, preferably from about 2 to about 12 g sodium sulphate/l of composition (electrolyte) in order to lower the solubility of lead sulphate in a battery cell. Aluminium hydroxide may also be added, preferably in an amount of from about 0.1 to about 0.5 wt% based on aluminium oxide. Other suitable additives that can be added include such as mentioned in US patent 6 218 052 to enhance battery performance. These components may be added either directly to the mixture of silica sol and mineral acid, or to either the mineral acid or silica sol directly before mixing thereof.

The invention also relates to a composition obtainable by the method as defined herein.

The invention also relates to a composition comprising a network of silica particles, in which the size of the (primary) silica particles making up the network, i.e. the particle size of a silica particle as single silica particle, is from about 2 to about 7, more preferably from about 3 to about 6, and most preferably from about 4 to about 5 nm. The composition further comprises a mineral acid as described herein. The size of the primary silica particle can be determined by the specific surface as measured by titration according to Sears (Journal of Analytical Chemistry, Volume 28, no.12, December 1956). However, the specific surface area measured by the technique described in Sears will be slightly underestimated since a portion of the surface of the silica particle is occupied by bonds/bridges to neighbouring silica particles in the network. The correction between the specific surface area of a primary particle and measured surface area of the gel is further discussed in The Chemistry of Silica (1979), p. 482 to p. 487, by Ralph K. Iler. The silica particles comprised in the composition suitably have a specific surface area from about 200 to about 1100, preferably from about 300 to about 1000, more preferably from about 400 to about 900, and most preferably from about 500 to 800 m²/g. The weight ratio of silica to mineral acid (counted as diluted mineral acid), in the network of silica, is suitably from about 1:100 to about 25:100, preferably from about 2:100 to about 11:100, more

preferably from about 2.5:100 to about 8:100, and most preferably from about 3:100 to about 6:100. The silica content of the composition suitably is from about 1 to about 20, preferably from about 2 to about 10, more preferably from about 2.5 to about 7.5, and most preferably from about 3 to about 6 wt%. A low silica content in the gel will result in lower internal resistance, and thus higher capacity as e.g. a gelled electrolyte in a battery. Preferably, the average pore diameter of the silica particles in the composition formed is from about 1 nm to about 100 nm, more preferably from about 5 nm to about 50 nm, and most preferably from about 10 nm to about 30 nm. Preferably, the pore volume of the silica particles in the composition is from about 0.4 to about 55, more preferably from about 1 to about 35, and most preferably from about 5 to about 20 cm³/g silica.

The invention also relates to the use of the composition as herein disclosed as a gelled electrolyte in traction batteries in e.g. submarines, wheelchairs, industrial trucks, and transport vehicles on golf courts; stand-by batteries in e.g. solar energy plants and telecommunication masts; and automotive batteries in e.g. start batteries and batteries for car electronics. These three groups of applications differ in their needs of battery capacity. Generally, it can be said that traction batteries need high capacity during a fairly long period of time, automotive batteries need very high capacity during a short period of time, and stand-by batteries need fairly low capacity during a long period of time.

The composition may also be used as a pickling gel, a binder of waste material, as an acid cleaning gel for surfaces and cavities and any other application where a gelled composition is desirable.

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the gist and scope of the present invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the claims. While the examples here below provide more specific details of the reactions, the following general principles may here be disclosed. The following examples will further illustrate how the described invention may be performed without limiting the scope of it.

All parts and percentages refer to part and percent by weight, if not otherwise stated.

Examples

The silica sols used in the examples are listed in table 1 below.

Table 1

5

Silica sol	1 (invention)	2 (reference)	3 (reference)
Specific surface area (m ² /g)	769	361	295
pH	10.5	10	10.5
Density (kg/dm ³) 20 °C	1.1	1.21	1.21
Silica Content (wt%)	14.9	30.3	30.1
Viscosity (cP)	8.2	7.0	8.6
S-value, Iler-Dalton (%)	33	96	52

10 The compositions of table 2 were prepared by use of the silica sols of table 1:
The procedure of obtaining the composition of the invention and the references was the following (which also can be found in table 2):

a) The concentrated sulphuric acid was diluted with water in a 250 ml beaker and cooled to room temperature.

15 b) The silica sols were mixed with the diluted sulphuric acid.

c) The temperature was measured in the silica sol-sulphuric acid mixture by means of a glass thermometer.

d) The gel time, i.e. the period of time from the starting point of mixing the silica sol and the mineral acid until a solid gel is obtained that does not flow when the beaker is tilted

20 90 °.

Table 2

Compo- sition No.	Conc. Sulphuric acid	H ₂ O	Silica Sol No.	Silica sol added (g)	Wt% SiO ₂	Gel time (min)	Temp. (exotherm reaction (°C)	Gel time (Isotherm reaction at 20 °C (min)	Total surface area of silica particles in m ² /g of composition
1	100 g	112 g	2	53	6	62	27	101	21.6
2	100 g	94.3 g	2	70.7	8	32	29	60	28.8
3	100 g	112 g	3	53	6	48	27	78	17.7
4	100 g	94.3 g	3	70.7	8	17	30	34	23.6
5	100 g	112 g	1	53	3	17	28	30	22.5
6	100 g	94.3 g	1	70.7	4	8	30	16	30

5

The gel time at 20 °C is a normalisation of the gel time at a temperature T at which the gelling took place. The gelling time at 20 °C can be calculated from the formula:

- 10 Gel time (T=20 °C) = Gel time (at T °C) * $2^{(T-20)/10}$, where T is the temperature in °C. As can be seen from table 2, the gel time is much shorter for samples 5 and 6 according to the present invention than the reference samples 1-4, both at reaction at the actual temperature and at the calculated temperature of 20 °C.

15

- 20 The gel strength was measured 24 hours after the formation of the gelled electrolyte. The gel strength was tested by dropping a lead bullet with a weight of 0.5 g, a diameter of 4.4 mm, from a height of 23 cm. The impact is shown in table 3 as penetration depth in mm in the gel which is a good measure of the gel strength.

Table 3

Composition no	Depth (mm)
1	8
2	1
3	8
4	1
5	1
6	0 (bounce)

5

It can be clearly seen that the compositions of the invention, i.e. no.5 and 6, show increased gel strength compared to the references 1-4. It is to be noted that compositions 5 and 6 comprise a lower amount of silica than compositions 1-4. Thus, the composition according to the invention can improve the mentioned effects even at a lower dosage of

10 silica sol than the references.

Claims

1. Method of preparing a composition comprising mixing a silica sol having an S-value from about 5 to about 50 % and a mineral acid.
- 5 2. Method according to claim 1, wherein the S-value is from about 8 to about 40 %.
3. Method according to claim 1 or 2, wherein the S-value is from about 12 to about 35 %.
4. Method according to any of claims 1-3, wherein the silica sol has a specific
10 surface area from about 400 to about 1200 m²/g.
5. Method according to any of claims 1-4, wherein the silica sol has a specific surface area from about 500 to about 1000 m²/g.
6. Method according to any of claims 1-5, wherein the silica sol has a specific surface area from about 600 to about 900 m²/g.
- 15 7. Method according to any of claims 1-6, wherein the mineral acid is sulphuric acid.
8. Method according to any of claims 1-6, wherein the mineral acid is hydrochloric acid, nitric acid, phosphoric acid, and mixtures thereof.
9. Method according to any of claims 1-8, wherein orthophosphoric acid and/or
20 sodium sulphate is further added.
10. Method according to any of claims 1-9, wherein the weight ratio of silica to mineral acid is from about 1:100 to about 25:100.
11. Method of producing a battery comprising providing a composition according to any of claims 1-10.
- 25 12. Composition obtainable by the method according to any of claims 1-10.
13. Composition comprising a network of silica particles and mineral acid, wherein the silica particles have a particle size of from about 2 to about 7 nm.
14. Composition according to claim 11 or 12, wherein the weight ratio of silica to mineral acid is from about 1:100 to about 25:100.
- 30 15. Use of a composition according to any of claims 11-13 as a gelled electrolyte in a battery.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M8/14 C01B33/142 H01M10/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 537 373 A (WANG, LIANXIANG; ZHENG, ANCHEN; ZHENG, SHUO; ZHENG, HANG) 21 April 1993 (1993-04-21) * see col.1, 1.54 - col.4, 14, claims * the whole document	1-15
X	& PATENT ABSTRACTS OF JAPAN vol. 1999, no. 07, 31 March 1999 (1999-03-31) & JP 05 121090 A (RIANKISAN WAN; ANCHEN ZEN; SHUO ZEN; HAN ZEN), 18 May 1993 (1993-05-18) abstract ----- -/--	1-15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Inte Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 91/07350 A (EKA NOBEL AB) 30 May 1991 (1991-05-30) cited in the application * see p.1, 1.30 - 33, p.4, 1..5 -.15, claims * the whole document	1-15
X	US 6 372 806 B1 (KEISER BRUCE A ET AL) 16 April 2002 (2002-04-16) * see col.2, 1.7 - 53, col..3, 1..25 -33, claims * the whole document	1-15
X	EP 0 736 922 A (COMPAGNIE EUROPEENNE D'ACCUMULATEURS; ACCUMULATEURENFABRIK SONNENSCHNEIN) 9 October 1996 (1996-10-09) * see p.2, 1.1 - 53, claims * the whole document	1-15
X	WO 95/07235 A (OLERUD, SVEIN) 16 March 1995 (1995-03-16) * see p.3, 1.14 - p.4, 1.9, claims * the whole document	1-15
Y	PATENT ABSTRACTS OF JAPAN vol. 017, no. 340 (E-1389), 28 June 1993 (1993-06-28) & JP 05 047410 A (JAPAN STORAGE BATTERY CO LTD), 26 February 1993 (1993-02-26) abstract	1-15
Y	WO 00/66491 A (AKZO NOBEL N.V; EKA CHEMICALS AB; PERSSON, MICHAEL; TOKARZ, MAREK; DAH) 9 November 2000 (2000-11-09) * see p.3, 1.18 - 20, claim 10 * the whole document	1-15
Y	WO 94/05596 A (EKA NOBEL AB) 17 March 1994 (1994-03-17) * see p.4, 1.4 - 37, claims * the whole document	1-15
Y	DE 33 24 740 A1 (CENTRAL GLASS CO.,LTD; CENTRAL GLASS CO., LTD., UBE, YAMAGUCHI, JP) 26 January 1984 (1984-01-26) * see p.14 - 34, examples ,claims * the whole document	1-15
Y	& PATENT ABSTRACTS OF JAPAN vol. 008, no. 098 (C-221), 9 May 1984 (1984-05-09) & JP 59 013620 A (CENTRAL GLASS KK), 24 January 1984 (1984-01-24) abstract	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int Application No
PCT/SE2004/001635

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0537373	A	21-04-1993	EP 0537373 A1 DE 69108396 D1 DE 69108396 T2	21-04-1993 27-04-1995 21-09-1995
WO 9107350	A	30-05-1991	SE 500387 C2 AR 243851 A1 AT 107608 T AU 628692 B2 AU 6733490 A BR 9007822 A CA 2067506 A1 CN 1115817 A ,C DE 69010210 D1 DE 69010210 T2 DK 491879 T3 EP 0491879 A1 ES 2055581 T3 FI 922056 A ,B, JP 4505314 T JP 5009368 B KR 9505762 B1 LT 445 A ,B LV 10227 A ,B NO 921848 A NZ 235963 A PT 95849 A ,B SE 8903753 A WO 9107350 A1 RU 2068809 C1 US 5643414 A US 5368833 A	13-06-1994 30-09-1993 15-07-1994 17-09-1992 13-06-1991 01-09-1992 09-05-1991 31-01-1996 28-07-1994 13-10-1994 07-11-1994 01-07-1992 16-08-1994 06-05-1992 17-09-1992 04-02-1993 30-05-1995 25-10-1994 20-10-1994 11-05-1992 26-05-1992 13-09-1991 10-05-1991 30-05-1991 10-11-1996 01-07-1997 29-11-1994
US 6372806	B1	16-04-2002	US 2003065041 A1 US 6372089 B1 US 6486216 B1	03-04-2003 16-04-2002 26-11-2002
EP 0736922	A	09-10-1996	DE 19513343 C1 DE 59602361 D1 EP 0736922 A1 US 5664321 A	10-10-1996 12-08-1999 09-10-1996 09-09-1997
WO 9507235	A	16-03-1995	NO 933168 A AT 161522 T AU 7666894 A BR 9407389 A CA 2171099 A1 CN 1133586 A DE 69407610 D1 DE 69407610 T2 EP 0720587 A1 ES 2113124 T3 FI 961018 A GR 3026299 T3 JP 9502688 T WO 9507235 A1 PL 313351 A1 US 5780005 A	07-03-1995 15-01-1998 27-03-1995 29-10-1996 16-03-1995 16-10-1996 05-02-1998 09-04-1998 10-07-1996 16-04-1998 02-05-1996 30-06-1998 18-03-1997 16-03-1995 24-06-1996 14-07-1998

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/SE2004/001635

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 05047410	A	26-02-1993	NONE
WO 0066491	A	09-11-2000	AU 758165 B2 20-03-2003
			AU 4789600 A 17-11-2000
			AU 766747 B2 23-10-2003
			AU 4789700 A 17-11-2000
			BR 0010238 A 19-03-2002
			BR 0010239 A 19-03-2002
			CA 2371492 A1 09-11-2000
			CA 2371494 A1 09-11-2000
			CN 1349479 A 15-05-2002
			CN 1349480 A 15-05-2002
			CZ 20013895 A3 15-05-2002
			CZ 20013915 A3 15-05-2002
			EP 1181244 A1 27-02-2002
			EP 1181245 A1 27-02-2002
			JP 2002543303 T 17-12-2002
			JP 2002543034 T 17-12-2002
			NZ 514752 A 30-01-2004
			NZ 514753 A 26-03-2004
			PL 351165 A1 24-03-2003
			PL 351201 A1 24-03-2003
			RU 2213053 C2 27-09-2003
			RU 2235683 C2 10-09-2004
			WO 0066491 A1 09-11-2000
			WO 0066492 A1 09-11-2000
			TW 527318 B 11-04-2003
			US 2002147240 A1 10-10-2002
			US 2003024671 A1 06-02-2003
			ZA 200108332 A 10-10-2002
			ZA 200108333 A 10-10-2002
			TW 568884 B 01-01-2004
WO 9405596	A	17-03-1994	SE 501214 C2 12-12-1994
			AT 138354 T 15-06-1996
			AU 667966 B2 18-04-1996
			AU 4988193 A 29-03-1994
			BR 9306878 A 08-12-1998
			CA 2141551 A1 17-03-1994
			CN 1084490 A ,C 30-03-1994
			DE 69302823 D1 27-06-1996
			DK 656872 T3 07-10-1996
			EP 0656872 A1 14-06-1995
			ES 2087767 T3 16-07-1996
			FI 950622 A 13-02-1995
			JP 2787377 B2 13-08-1998
			JP 8502016 T 05-03-1996
			MX 9305272 A1 28-02-1994
			NO 950738 A 27-02-1995
			NZ 255615 A 27-11-1995
			RU 2081060 C1 10-06-1997
			SE 9202502 A 01-03-1994
			WO 9405596 A1 17-03-1994
			US 5603805 A 18-02-1997
DE 3324740	A1	26-01-1984	JP 1459603 C 28-09-1988
			JP 59013620 A 24-01-1984
			JP 63006484 B 10-02-1988

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int

Application No

PCT/SE2004/001635

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3324740	A1	GB 2125780 A ,B	14-03-1984